

Virial expansion of molecular Brownian motion versus tales of “statistical independency”

Yu E Kuzovlev

Donetsk Institute for Physics and Technology of NASU, 83114 Donetsk, Ukraine

E-mail: kuzovlev@kinetic.ac.donetsk.ua

Abstract. Basing on main principles of statistical mechanics only, an exact virial expansion for path probability distribution of molecular Brownian particle in a fluid is derived which connects response of the distribution to perturbations of the fluid and statistical correlations of its molecules with Brownian particle. The expansion implies that (i) spatial spread of these correlations is finite, (ii) this is inconsistent with Gaussian distribution involved by the “molecular chaos” hypothesis, and (iii) real path distribution possesses power-law long tails. This means that actual Brownian path never can be disjointed into statistically independent fragments, even in the Boltzmann-Grad gas, but behaves as if Brownian particle’s diffusivity undergoes scaleless low-frequency fluctuations.

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“‘God does not play dice’” (A. Einstein)

1. Introduction

Molecules in gases and liquids, or free electrons and holes in crystals, etc., can be treated as “small Brownian particles” (BP) since their thermal motion undoubtedly is “not less random” than motion of the R. Brown’s pollen suspended in water. Therefore, seemingly, the A. Einstein’s reasonings [1, 2] can be applied to a small molecular-size BP too, again producing the diffusion equation for probability density of BP’s position. The diffusion equation, in its turn, implies that probability distribution, $V_0(t, \Delta \mathbf{R})$, of displacement of BP, $\Delta \mathbf{R}$, during time interval $(0, t)$, at long enough t tends to the Gaussian distribution:

$$V_0(t, \Delta \mathbf{R}) \rightarrow V_G(t, \Delta \mathbf{R}) = (4\pi Dt)^{-3/2} \exp(-\Delta \mathbf{R}^2/4Dt) \quad (1)$$

Formally, Einstein in [1] assumed that $\Delta \mathbf{R}$ consists of many increments which are *statistically independent* in the sense of the probability theory. Thus, from statistical point of view, his result is equivalent to the “*law of large numbers*” discovered by J. Bernoulli almost two centuries earlier [3].

The idea of *statistical independency*, in the form of the “Stosszahlansatz”, or “molecular chaos hypothesis”, was also taken by L. Boltzmann as a principle of his molecular-kinetic theory of gases [4]. Later in [5] N. Bogolyubov imparted it, after non-principal modification, to a theory based on the Bogolyubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy of equations [5, 6, 7, 8, 9]. It was violence against own brainchild, because the BBGKY equations are quite all-sufficient ones and do not need in any add-on (except natural initial conditions, of course). Unfortunately, the violence lasts up to now: various (higher-order, non-local, etc.) generalizations of the Boltzmann kinetic equation to relatively dense gases [6, 7, 8, 9] all the same rest upon one or another variant of the “Stosszahlansatz”. Although an attempt to break this tradition was made in [10] (see also [11]).

At same time of the forties, N. Krylov in his book [12] (first published in 1950 in Russian) argued that probability-theoretic concepts under use in modern kinetics generally are incompatible with principles of statistical mechanics. Especially he emphasized fallacy of common opinions that “*probabilities do exist regardless of a theoretical construct and full-scale experiments*” and that “*obviously independent phenomena should possess independent probability distributions*” (italics mark brief citations from [12]). According to Krylov, “physical independency” of events in reality does not mean their “*statistical independency*” in theory.

At present, survivability of the prejudices disclosed by Krylov is the only excuse of the “Stosszahlansatz” or similar conjectures. They gave rise to conviction that in the limit of “Boltzmann-Grad gas” (“infinitely dilute gas”) infinite BBGKY hierarchy reduces to the single Boltzmann equation, i.e. the latter presents exact gas kinetics. If such was the case, then random walk of a molecular BP (e.g. test or marked gas atom) would be made of many *statistically independent* events and pieces. Then the “*law of large numbers*” is in effect, and probability distribution of the Brownian path $\Delta \mathbf{R}$ in thermodynamically equilibrium gas should have Gaussian asymptotic (1).

But this is not true! In fact, as we will show, $V_0(t, \Delta \mathbf{R})$ has essentially non-Gaussian asymptotic possessing power-law tails at $\Delta \mathbf{R}^2/4Dt > 1$ instead of the exponential ones, even in equilibrium gas under the Boltzmann-Grad limit (BGL).

Hence, N. Krylov was right, and *statistical independency* of colliding molecules or *statistical independency* of different pieces of Brownian trajectory, etc., like *statistical independency* of mathematical dice tosses, exists in imagination only but not in physical reality. If reinterpreting the well-known words said by Einstein, one can say that he was playing dice in [1] but God does not play dice.

A substantiation of these statements below (see also [13, 14, 15]) will be done “at very thermodynamical level” basing on only determinism and reversibility of Hamiltonian microscopic dynamics and besides general notions about many-particle distribution functions and correlation functions [6, 7, 8] and main fluid properties.

In spite of so abstract approach, remarkably, our conclusions will be in full qualitative agreement with result obtained in [16] by means of crucial approximation of the BBGKY hierarchy and then its direct solving under BGL:

$$V_0(t, \Delta \mathbf{R}) \rightarrow (4\pi Dt)^{-3/2} \Gamma(7/2) (1 + \Delta \mathbf{R}^2/4Dt)^{-7/2} \quad (2)$$

(in [16] designation W_1 was used in place of V_0). The diffusivity D here, as well as in (1), is defined by $\int \Delta \mathbf{R}^2 V_0(t, \Delta \mathbf{R}) d\Delta \mathbf{R} \rightarrow 6Dt$, while the arrow everywhere denotes asymptotic at t much greater than BP’s mean free-flight time.

Our plan is as follows. In the beginning, a kind of virial expansion for $V_0(t, \Delta \mathbf{R})$ is derived. It connects, from one hand, first- and higher-order derivatives of $V_0(t, \Delta \mathbf{R})$

with respect to gas density and, from the other hand, pair and many-particle joint correlation functions (CF) of BP and gas. The CF in their turn are definitely related to usual distribution functions (DF). Since the latter by their sense are non-negative, the virial expansion results in a series of differential inequalities to be satisfied by $V_0(t, \Delta \mathbf{R})$. The first of them, eventually, restricts a steepness of $V_0(t, \Delta \mathbf{R})$'s tails and clearly forbids their exponentially fast decrease. At the end of the paper, its relation to the problem of $1/f$ noise is commented.

2. Virial expansion of Brownian path probability distribution

2.1. Full-scale experiments and fluctuation-dissipation relations

We will consider a system consisting of $N \gg 1$ atoms in volume Ω plus one more corpuscular “Brownian particle” (BP), under the thermodynamical limit: $N \rightarrow \infty$, $\Omega \rightarrow \infty$, $N/\Omega = \nu_0 = \text{const}$. Initially, at time $t = 0$, position of BP $\mathbf{R}(t)$ is definitely known. We are interested in the already mentioned distribution $V_0(t, \Delta \mathbf{R})$ of consequent BP's path $\Delta \mathbf{R} = \mathbf{R}(t) - \mathbf{R}(0)$. Especially (see Introduction), in thermodynamically equilibrium Boltzmann-Grad gas where *a fortiori* any “collective” or “hydrodynamic” contributions to chaotic motion of particles disappear. At the same time, as far as possible, we want to take in mind also finite-density and non-equilibrium gas and even liquid.

Instead of “art of decomposition” of BP's path into some constituent parts and “art of conjecturing” about their “probabilities”, we want to follow N. Krylov (see Introduction) and consider a set of mental “full-scale experiments” to see how BP's path as a whole is influenced by artificial controllable perturbations of both gas and BP. Thus we involve into consideration statistical correlations between BP's path and gas atoms. At that, the only “probability” to be specified (at our own choosing, without any conjectures) is initial probabilistic measure in the space of states of the system. To find other “probabilities”, one should analyze a flow of this measure according to the Liouville equation or equivalent BBGKY equations. But a great deal can be found from time reversibility of this flow only which is expressed e.g. by the “generalized fluctuation-dissipation relations” (FDR) [17, 18, 19].

Let, firstly, $\mathbf{q} = \{\mathbf{R}, \mathbf{r}_1, \dots, \mathbf{r}_N\}$ and $\mathbf{p} = \{\mathbf{P}, \mathbf{p}_1, \dots, \mathbf{p}_N\}$ are (canonical) coordinates and momentums of our system, and $H(\mathbf{q}, \mathbf{p})$ its Hamiltonian in absence of its perturbations, so that $H(\mathbf{q}, -\mathbf{p}) = H(\mathbf{q}, \mathbf{p})$. Secondly, the initial probabilistic measure, $\rho_{in}(\mathbf{q}, \mathbf{p})$, is the equilibrium canonical one corresponding to this Hamiltonian, that is $\rho_{in}(\mathbf{q}, \mathbf{p}) = \rho_{eq}(\mathbf{q}, \mathbf{p}) \propto \exp[-H(\mathbf{q}, \mathbf{p})/T]$ (omitting a normalization factor). Thirdly, suppose possibility that BP is perturbed by a constant external force \mathbf{f} which is sharply switched on at $t = 0$, thus at $t > 0$ changing the Hamiltonian to $H(t, \mathbf{q}, \mathbf{p}) = H(\mathbf{q}, \mathbf{p}) - \mathbf{f} \cdot \mathbf{R}$.

Then we can either directly write according to works [17] or [19] or derive by their methods, like in [15], the very particular but useful enough FDR as follows:

$$\begin{aligned} \langle A(\mathbf{q}(t), \mathbf{p}(t)) B(\mathbf{q}(0), \mathbf{p}(0)) e^{-\mathcal{E}(t)/T} \rangle_0 = \\ = \langle B(\mathbf{q}(t), -\mathbf{p}(t)) A(\mathbf{q}(0), -\mathbf{p}(0)) \rangle_0 \end{aligned} \quad (3)$$

Here $\mathcal{E}(t) = \mathbf{f} \cdot [\mathbf{R}(t) - \mathbf{R}(0)]$ is work made by the external force during time interval $(0, t)$, $A(\mathbf{q}, \mathbf{p})$ and $B(\mathbf{q}, \mathbf{p})$ are “arbitrary functions”, the angle brackets $\langle \dots \rangle_0$ designate averaging over statistical ensemble of phase trajectories of the system corresponding to the equilibrium Gibbs ensemble of their initial conditions, and T

is initial temperature of the system (or, to be precise, of the ensemble). At any concrete trajectory, of course, $\mathbf{q}(t)$ and $\mathbf{p}(t)$ represent solutions to Hamilton equations corresponding to the Hamiltonian $H(t, \mathbf{q}, \mathbf{p}) = H(\mathbf{q}, \mathbf{p}) - \mathbf{f} \cdot \mathbf{R}$ and hence are some functions of the force \mathbf{f} . The equality (3) holds also if BP has internal degrees of freedom. In absence of external force, when $\mathcal{E}(t) = 0$, it is so obvious that even does not need in a proof.

Further it is sufficient to confine ourselves by such particular choice as

$$\begin{aligned} A(\mathbf{q}, \mathbf{p}) &= \delta(\mathbf{R} - \mathbf{R}') , \\ B(\mathbf{q}, \mathbf{p}) &= \Omega \delta(\mathbf{R} - \mathbf{R}_0) \delta(\mathbf{P} - \mathbf{P}_0) \exp \left[- \sum_{j=1}^N U(\mathbf{r}_j, \mathbf{p}_j) / T \right] \\ &= \Omega \delta(\mathbf{R} - \mathbf{R}_0) \delta(\mathbf{P} - \mathbf{P}_0) \prod_{j=1}^N [1 + \psi(\mathbf{r}_j, \mathbf{p}_j)] , \end{aligned} \quad (4)$$

where $\psi(\mathbf{r}, \mathbf{p}) \equiv \exp[-U(\mathbf{r}, \mathbf{p})/T] - 1$.

2.2. Generating functional of distribution functions

Under choice (4) in the thermodynamical limit right-hand side of (3) takes form

$$\langle B(\mathbf{q}(t), -\mathbf{p}(t)) A(\mathbf{q}(0), -\mathbf{p}(0)) \rangle_0 = \mathcal{F}\{t, \mathbf{R}_0, -\mathbf{P}_0, \psi | \mathbf{R}'\} \quad (5)$$

where

$$\begin{aligned} \mathcal{F}\{t, \mathbf{R}_0, \mathbf{P}_0, \psi | \mathbf{R}'\} &\equiv V_0(t, \mathbf{R}_0, \mathbf{P}_0 | \mathbf{R}') + \\ &+ \sum_{n=1}^{\infty} \frac{\nu_0^n}{n!} \int_{r \times p}^n F_n(t, \mathbf{R}_0, \mathbf{r}_1 \dots \mathbf{r}_n, \mathbf{P}_0, \mathbf{p}_1 \dots \mathbf{p}_n | \mathbf{R}') \prod_{j=1}^n \psi(\mathbf{r}_j, -\mathbf{p}_j) \end{aligned} \quad (6)$$

Here symbol $\int_{r \times p}^n$ denotes integration over n coordinates $\mathbf{r}_1 \dots \mathbf{r}_n$ and momentums $\mathbf{p}_1 \dots \mathbf{p}_n$; function $V_0(t, \mathbf{R}_0, \mathbf{P}_0 | \mathbf{R}')$ is conditional probability density of finding BP at $t \geq 0$ at point \mathbf{R}_0 with momentum \mathbf{P}_0 under condition that BP had started at $t = 0$ from point \mathbf{R}' , and $F_n(t, \mathbf{R}_0, \mathbf{r}_1 \dots \mathbf{r}_n, \mathbf{P}_0, \mathbf{p}_1 \dots \mathbf{p}_n | \mathbf{R}')$ is joint conditional probability density of this event and simultaneously finding some atoms at points \mathbf{r}_j with momentums \mathbf{p}_j under the same condition.

In respect to atoms, all the F_n are complete analogues of standardly defined non-normalized many-particle DF of infinite gas [5]. Instead of normalization, “asymptotic uncoupling” of inter-particle correlations takes place:

$$\begin{aligned} F_n(\dots \mathbf{r}_k \dots \mathbf{p}_k \dots) &\rightarrow F_{n-1}(\dots \mathbf{r}_{k-1}, \mathbf{r}_{k+1} \dots \mathbf{p}_{k-1}, \mathbf{p}_{k+1} \dots) G_m(\mathbf{p}_k) , \\ F_1(t, \mathbf{R}_0, \mathbf{P}_0, \mathbf{r}_1, \mathbf{p}_1 | \mathbf{R}') &\rightarrow V_0(t, \mathbf{R}_0, \mathbf{P}_0 | \mathbf{R}') G_m(\mathbf{p}_1) , \end{aligned}$$

when $\mathbf{r}_k \rightarrow \infty$ and $\mathbf{r}_1 \rightarrow \infty$, respectively, with $G_m(\mathbf{p})$ being equilibrium Maxwellian distribution of atomic momentum, $G_m(\mathbf{p}) = (2\pi T m)^{-3/2} \exp(-\mathbf{p}^2/2Tm)$, and m atomic mass. But, because of initial localization of BP, in respect to BP's variables all the DF are normalized in literal sense. In particular,

$$\begin{aligned} \int V_0(t, \mathbf{R}_0, \mathbf{P}_0 | \mathbf{R}') d\mathbf{P}_0 &= V_0(t, \mathbf{R}_0 - \mathbf{R}') , \\ \int V_0(t, \mathbf{R}_0 - \mathbf{R}') d\mathbf{R}_0 &= 1 \end{aligned}$$

In respect to ψ , expression $\mathcal{F}\{t, \mathbf{R}_0, \mathbf{P}_0, \psi | \mathbf{R}'\}$ represents generating functional for these DF quite similar to the functional originally introduced by Bogolyubov [5].

By definition of the average $\langle \dots \rangle_0$, all the DF represent BP in initially thermodynamically equilibrium gas (or, to be precise, in equilibrium Gibbs ensemble of identical systems “gas plus BP”). Correspondingly, initial conditions to them are

$$V_0(0, \mathbf{R}_0, \mathbf{P}_0 | \mathbf{R}') = \delta(\mathbf{R}_0 - \mathbf{R}') G_M(\mathbf{P}_0) , \quad (7)$$

$$\begin{aligned}
F_n(0, \mathbf{R}_0, \mathbf{r}_1 \dots \mathbf{r}_n, \mathbf{P}_0, \mathbf{p}_1 \dots \mathbf{p}_n | \mathbf{R}') &= \\
&= F_n^{(eq)}(\mathbf{r}_1 \dots \mathbf{r}_n | \mathbf{R}_0) \delta(\mathbf{R}_0 - \mathbf{R}') G_M(\mathbf{P}_0) \prod_{j=1}^n G_m(\mathbf{p}_j) , \\
\mathcal{F}\{0, \mathbf{R}_0, \mathbf{P}_0, \psi | \mathbf{R}'\} &= \delta(\mathbf{R}_0 - \mathbf{R}') G_M(\mathbf{P}_0) \mathcal{F}^{(eq)}\{\phi | \mathbf{R}_0\} ,
\end{aligned} \tag{8}$$

where

$$\begin{aligned}
\phi(\mathbf{r}) &= \int \psi(\mathbf{r}, -\mathbf{p}) G_m(\mathbf{p}) d\mathbf{p} = \int \psi(\mathbf{r}, \mathbf{p}) G_m(\mathbf{p}) d\mathbf{p} , \\
\mathcal{F}^{(eq)}\{\phi | \mathbf{R}_0\} &\equiv 1 + \sum_{n=1}^{\infty} \frac{\nu_0^n}{n!} \int_r^n F_n^{(eq)}(\mathbf{r}_1 \dots \mathbf{r}_n | \mathbf{R}_0) \prod_{j=1}^n \phi(\mathbf{r}_j) ,
\end{aligned} \tag{9}$$

functions $F_n^{(eq)}(\mathbf{r}_1 \dots \mathbf{r}_n | \mathbf{R}_0)$ are conditional equilibrium DF of gas under fixed position of BP, $\mathcal{F}^{(eq)}\{\phi | \mathbf{R}_0\}$ is their generating functional, and M means BP's mass.

Of course, all the DF possess translational invariance. Notice also that, firstly, ratios F_n/V_0 represent conditional DF of gas under condition that both initial position of BP and its current state are known. Secondly, at least under condition

$$\int |\phi(\mathbf{r})| d\mathbf{r} < \infty \tag{10}$$

the infinite series are converging and hence the functionals are well defined.

2.3. BP-gas correlations

In absence of the external force ($\mathbf{f} = 0$) just listed DF describe Brownian motion in gas which all the time remains in exact thermodynamical equilibrium. Nevertheless, at $t > 0$ not only F_n but conditional DF F_n/V_0 too are constantly changing along with V_0 . In principle, their joint evolution is unambiguously prescribed by the BBGKY equations together with initial conditions (7) and (8) [10, 11, 15, 16]. At that, differences

$$F_n(t, \mathbf{R}_0, \mathbf{r}_1 \dots \mathbf{r}_n, \mathbf{P}_0, \mathbf{p}_1 \dots \mathbf{p}_n | \mathbf{R}') - V_0(t, \mathbf{R}_0, \mathbf{P}_0 | \mathbf{R}') F_n^{(eq)}(\mathbf{r}_1 \dots \mathbf{r}_n | \mathbf{R}_0) \prod_j G_m(\mathbf{p}_j)$$

reflect additional specific statistical correlations between BP and gas which arise just due to evolution of $V_0(t, \mathbf{R}_0, \mathbf{P}_0 | \mathbf{R}')$. Roughly, an origin of their specificity is that they are correlations of a current gas state with previous BP's path accumulated during all the time interval $(0, t)$. By this reason we can characterize them as “historical correlations”.

By tradition, any additions to equilibrium (or quasi-equilibrium) DF are termed “correlation functions” (CF) [7, 5, 8]. We will apply this term also to functions what describe the “historical correlations”. Let us designate CF as $V_n(t, \mathbf{R}_0, \mathbf{r}_1 \dots \mathbf{r}_n, \mathbf{P}_0, \mathbf{p}_1 \dots \mathbf{p}_n | \mathbf{R}')$ and introduce them through their generating functional:

$$\mathcal{F}\{t, \mathbf{R}_0, \mathbf{P}_0, \psi | \mathbf{R}'\} = \mathcal{F}^{(eq)}\{\phi | \mathbf{R}_0\} \mathcal{V}\{t, \mathbf{R}_0, \mathbf{P}_0, \psi | \mathbf{R}'\} , \tag{11}$$

where $\phi = \phi(\mathbf{r})$ is expressed through $\psi = \psi(\mathbf{r}, \mathbf{p})$ by formula (9), and

$$\begin{aligned}
\mathcal{V}\{t, \mathbf{R}_0, \mathbf{P}_0, \psi | \mathbf{R}'\} &= V_0(t, \mathbf{R}_0, \mathbf{P}_0 | \mathbf{R}') + \\
&+ \sum_{n=1}^{\infty} \frac{\nu_0^n}{n!} \int_{r \times p}^n V_n(t, \mathbf{R}_0, \mathbf{r}_1 \dots \mathbf{r}_n, \mathbf{P}_0, \mathbf{p}_1 \dots \mathbf{p}_n | \mathbf{R}') \prod_{j=1}^n \psi(\mathbf{r}_j, -\mathbf{p}_j)
\end{aligned} \tag{12}$$

According to this definition, in particular,

$$\begin{aligned} F_1(t, \mathbf{R}_0, \mathbf{r}_1, \mathbf{P}_0, \mathbf{p}_1 | \mathbf{R}') &= \\ &= V_0(t, \mathbf{R}_0, \mathbf{P}_0 | \mathbf{R}') F_1^{(eq)}(\mathbf{r}_1 | \mathbf{R}_0) G_m(\mathbf{p}_1) + V_1(t, \mathbf{R}_0, \mathbf{r}_1, \mathbf{P}_0, \mathbf{p}_1 | \mathbf{R}') , \end{aligned} \quad (13)$$

where function V_1 represents pair “historical” correlation between BP and atoms.

In view of the asymptotic decoupling of inter-particle correlations, it is clear that all the CF disappear in initial equilibrium state, $V_n(0, \dots) = 0$ at $n > 0$, as well as far from BP, i.e. $V_n(t, \dots \mathbf{r}_k \dots) \rightarrow 0$ at $\mathbf{r}_k \rightarrow \infty$.

2.4. Main relation between correlation functions and response of Brownian path to gas perturbations

Now let us introduce $\Psi(\mathbf{q}, \mathbf{p}) = \Omega \delta(\mathbf{R} - \mathbf{R}_0) \prod_j [1 + \psi(\mathbf{r}_j, \mathbf{p}_j)]$ and, under the choice (4), consider left side of (3) rewriting it as

$$\begin{aligned} \langle A(\mathbf{q}(t), \mathbf{p}(t)) B(\mathbf{q}(0), \mathbf{p}(0)) e^{-\mathcal{E}(t)/T} \rangle_0 &= \\ &= \langle \Psi(\mathbf{q}, \mathbf{p}) \rangle_0 \langle \delta(\mathbf{R}(t) - \mathbf{R}') \delta(\mathbf{P}(0) - \mathbf{P}_0) \rangle e^{-\mathbf{f} \cdot [\mathbf{R}' - \mathbf{R}_0]/T} , \end{aligned} \quad (14)$$

where the brackets $\langle \dots \rangle$ are defined by

$$\langle \Phi \rangle \equiv \langle \Phi \Psi(\mathbf{q}, \mathbf{p}) \rangle_0 / \langle \Psi(\mathbf{q}, \mathbf{p}) \rangle_0$$

with Φ being arbitrary functional of the system’s phase trajectory.

Evidently, $\langle \dots \rangle$ in fact represents averaging over new statistical ensemble of initial conditions, with new probabilistic measure

$$\rho_{in}(\mathbf{q}, \mathbf{p}) \propto \rho_{eq}(\mathbf{q}, \mathbf{p}) \Psi(\mathbf{q}, \mathbf{p}) \propto \delta(\mathbf{R} - \mathbf{R}_0) \exp[-H(\mathbf{q}, \mathbf{p})/T - \sum_j U(\mathbf{q}_j, \mathbf{p}_j)/T]$$

(again normalizing coefficients are omitted). Formally this measure can be viewed as also a canonical equilibrium one but in presence of generalized (momenta-dependent) external potential $U(\mathbf{q}, \mathbf{p}) = -T \ln[1 + \psi(\mathbf{q}, \mathbf{p})]$. In fact, of course, this is thermodynamically non-equilibrium measure since system’s Hamiltonian does not include such potential. Hence, second right-hand average in (14) is nothing but

$$\langle \delta(\mathbf{R}(t) - \mathbf{R}') \delta(\mathbf{P}(0) - \mathbf{P}_0) \rangle = V\{t, \mathbf{R}' | \psi, \mathbf{R}_0, \mathbf{P}_0\} G_M(\mathbf{P}_0) , \quad (15)$$

where $V\{t, \mathbf{R}' | \psi, \mathbf{R}_0, \mathbf{P}_0\}$ is conditional probability density of finding BP at point \mathbf{R}' under conditions that initially, at $t = 0$, it was located at point \mathbf{R}_0 with momentum \mathbf{P}_0 while gas was in such non-equilibrium spatially-nonuniform state what would be equilibrium under external potential $U(\mathbf{q}, \mathbf{p})$. Noticing, besides, that

$$\langle \Psi(\mathbf{q}, \mathbf{p}) \rangle_0 = \mathcal{F}^{(eq)}\{\phi | \mathbf{R}_0\} ,$$

(again with ϕ expressed through ψ by (9)), we can write

$$\begin{aligned} \langle A(\mathbf{q}(t), \mathbf{p}(t)) B(\mathbf{q}(0), \mathbf{p}(0)) e^{-\mathcal{E}(t)/T} \rangle_0 &= \\ &= V\{t, \mathbf{R}' | \psi, \mathbf{R}_0, \mathbf{P}_0\} G_M(\mathbf{P}_0) e^{-\mathbf{f} \cdot [\mathbf{R}' - \mathbf{R}_0]/T} \mathcal{F}^{(eq)}\{\phi | \mathbf{R}_0\} \end{aligned} \quad (16)$$

Equivalently, instead of the artificial external potential $U(\mathbf{q}, \mathbf{p})$, the non-equilibrium ensemble which has arisen can be characterized by corresponding conditional mean densities of atoms in the μ -space and coordinate space,

$$\begin{aligned} \mu\{\mathbf{r}, \mathbf{p} | \psi, \mathbf{R}_0\} &\equiv \langle \sum_j \delta(\mathbf{r}_j - \mathbf{r}) \delta(\mathbf{p}_j - \mathbf{p}) \rangle = \nu\{\mathbf{r} | \phi, \mathbf{R}_0\} G_m(\mathbf{p}) \frac{1 + \psi(\mathbf{r}, \mathbf{p})}{1 + \phi(\mathbf{r})} , \\ \nu\{\mathbf{r} | \phi, \mathbf{R}_0\} &\equiv \langle \sum_j \delta(\mathbf{r}_j - \mathbf{r}) \rangle = [1 + \phi(\mathbf{r})] \frac{\delta \ln \mathcal{F}^{(eq)}\{\phi | \mathbf{R}_0\}}{\delta \phi(\mathbf{r})} \end{aligned} \quad (17)$$

At that, $\mu\{\mathbf{r}, \mathbf{p}|\psi, \mathbf{R}_0\}/\nu_0$ has the sense of initial one-particle DF of atoms.

At last, combining formulas (3), (5), (11), (12) and (16), we come to formally exact relation

$$\begin{aligned} & V\{t, \mathbf{R}'|\psi, \mathbf{R}_0, \mathbf{P}_0\} G_M(\mathbf{P}_0) e^{-\mathbf{f}\cdot[\mathbf{R}'-\mathbf{R}_0]/T} = \\ & = V_0(t, \mathbf{R}_0, -\mathbf{P}_0|\mathbf{R}') + \sum_{n=1}^{\infty} \frac{\nu_0^n}{n!} \int_{r \times p} V_n(t, \mathbf{R}_0, \mathbf{r}_1 \dots \mathbf{r}_n, -\mathbf{P}_0, \mathbf{p}_1 \dots \mathbf{p}_n|\mathbf{R}') \prod_{j=1}^n \psi(\mathbf{r}_j, -\mathbf{p}_j) \end{aligned} \quad (18)$$

It connects, from one (left) hand, probability distribution of BP's path in initially non-equilibrium nonuniform gas and, from the other (right) hand, probability distribution of BP's path, along with generating functional of correlations between this previously accumulated path and current BP's environment, in initially equilibrium uniform gas. In case $\mathbf{f} = 0$, therefore, right-hand side of (18) represents wholly equilibrium Brownian motion.

In other words, relation (18) connects two sorts of “full-scale experiments”: one on susceptibility of Brownian motion to perturbations of medium where it takes place, and another on its correlations with thermal fluctuations in the medium. In such sense, (18) is typical generalized FDR or “generalized Onsager relation”.

At $\psi(\mathbf{r}, \mathbf{p}) = 0$, clearly, (18) turns into

$$V_0(t, \mathbf{R}'|\mathbf{R}_0, \mathbf{P}_0) G_M(\mathbf{P}_0) e^{-\mathbf{f}\cdot[\mathbf{R}'-\mathbf{R}_0]/T} = V_0(t, \mathbf{R}_0, -\mathbf{P}_0|\mathbf{R}') , \quad (19)$$

where $V_0(t, \mathbf{R}'|\mathbf{R}_0, \mathbf{P}_0)$ is density of probability to find BP (in the same gas as on the left) at point \mathbf{R}' under condition that it started from point \mathbf{R}_0 with momentum \mathbf{P}_0 . Integration over this momentum yields the classical FDR [18, 19, 21, 22]

$$V_0(t, \Delta\mathbf{R}) e^{-\mathbf{f}\cdot\Delta\mathbf{R}/T} = V_0(t, -\Delta\mathbf{R}) , \quad (20)$$

where $\Delta\mathbf{R} \equiv \mathbf{R}' - \mathbf{R}_0$ and

$$V_0(t, \mathbf{R}_0 - \mathbf{R}') = \int V_0(t, \mathbf{R}_0, \mathbf{P}_0|\mathbf{R}') d\mathbf{P}_0$$

Of course, all the DF and CF are dependent on the mean gas density ν_0 (and on the force \mathbf{f} if any) but for brevity in (18), as well as before it and almost everywhere below, corresponding arguments are omitted.

2.5. Quasi-uniform gas perturbations, spatial correlations and virial expansion

Let, firstly, the gas perturbation does not change velocity distribution of atoms, that is represents pure density perturbation, $\psi(\mathbf{r}, \mathbf{p}) = \phi(\mathbf{r})$. Secondly, $\phi(\mathbf{r}) = \phi = \text{const}$ inside some sphere $|\mathbf{r} - \mathbf{R}_0| < \xi$ and vanishes outside it in some suitable way (it should be underlined that nothing impedes choosing perturbations to be correlated with the point \mathbf{R}_0). Since, according to (10), $\phi(\mathbf{r})$ is absolutely integrable, radius ξ must be finite. But it can be as large as we want. At that, factual perturbation of gas equilibrium initially is located at $|\mathbf{r} - \mathbf{R}_0| > \xi$.

For example, we may take $\xi = k v_s t_0$, where v_s is speed of sound in our gas (or liquid), t_0 is maximal duration of our “full-scale experiments”, and $k > 2$. Then, if the external force is not too strong (so that velocity of BP's drift induced by the external force is small as compared with v_s), we can be sure that at $t < t_0$ the Brownian motion mentioned in left part of (18) practically takes place in equilibrium uniform gas with a constant mean density $\nu = \text{const}$ what corresponds to $\phi = \text{const}$. Indeed, under mentioned conditions $|\mathbf{R}(t) - \mathbf{R}(0)| < v_s t$ while radial approach of

inner front of the gas perturbation (let even Mach front) to the point $\mathbf{R}(0) = \mathbf{R}_0$ is not greater than $v_s t$. Hence, undoubtedly BP does not feel the front and moves as it was in spatially uniform (and thus equilibrium) media at least till $t < t_0$. This can be named “quasi-uniform perturbation” of gas.

Now, at $t < t_0$, in fact both parts of (18) describe Brownian motions in (initially) uniform equilibrium gases but with different values of density. On the right it is ν_0 while on the left it equals to $\nu\{\mathbf{r}|\phi, \mathbf{R}_0\}$ taken far from BP, at $|\mathbf{r} - \mathbf{R}_0| \gg r_B$, with r_B being radius of pair interaction between BP and atoms. We will denote this value simply as ν . According to (17), it is definite function of ϕ and the seed density ν_0 :

$$\begin{aligned} \nu = \nu(\nu_0, \phi) = \nu_0 (1 + \phi) \{ & 1 + \nu_0 \phi \int [F_2^{(eq)}(\mathbf{r}) - 1] + \\ & + \frac{\nu_0^2 \phi^2}{2} \int_r^2 [F_3^{(eq)}(\mathbf{r}_1, \mathbf{r}_2, 0) - F_2^{(eq)}(\mathbf{r}_1) - F_2^{(eq)}(\mathbf{r}_2) - F_2^{(eq)}(\mathbf{r}_1 - \mathbf{r}_2) + 2] + \dots \} \end{aligned} \quad (21)$$

Here $F_2^{(eq)}(\mathbf{r})$ and $F_3^{(eq)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ are standard pair and triple DF of equilibrium gas with density ν_0 (i.e. functions what follow from $F_n^{(eq)}(\mathbf{r}_1 \dots \mathbf{r}_n | \mathbf{R}_0)$ at $\mathbf{R}_0 \rightarrow \infty$).

Correspondingly, the functional $V\{t, \mathbf{R}'|\phi, \mathbf{R}_0, \mathbf{P}_0\}$ simplifies to mere function, and, integrating left side of (18) over \mathbf{P}_0 , for $t < t_0$ we can write

$$\int V\{t, \mathbf{R}'|\phi, \mathbf{R}_0, \mathbf{P}_0\} G_M(\mathbf{P}_0) d\mathbf{P}_0 = V_0(t, \mathbf{R}' - \mathbf{R}_0; \nu),$$

where V_0 has exactly the same sense as V_0 on the right-hand side of (18) (after its integration over \mathbf{P}_0), and we introduced the density argument ν , so that

$$V_0(t, \mathbf{R}_0 - \mathbf{R}'; \nu = \nu_0) = V_0(t, \mathbf{R}_0 - \mathbf{R}')$$

On right-hand side of (18), under the formulated conditions, *a fortiori* none correlations between BP and gas might propagate out of the sphere $|\mathbf{r} - \mathbf{R}_0| < \xi$. Therefore in all the integrals $\phi(\mathbf{r})$ can be replaced by the constant. Consequently, relation (18), after its integration over \mathbf{P}_0 , transforms into

$$V_0(t, \Delta\mathbf{R}; \nu(\nu_0, \psi)) e^{-\mathbf{f} \cdot \Delta\mathbf{R}/T} = V_0(t, -\Delta\mathbf{R}; \nu_0) + \sum_{n=1}^{\infty} \frac{\phi^n}{n!} V_n(t, -\Delta\mathbf{R}; \nu_0) \quad (22)$$

functions V_n at $n > 0$ defined by

$$V_n(t, \mathbf{R}_0 - \mathbf{R}'; \nu_0) = \nu_0^n \int_{r \times p}^n \int V_n(t, \mathbf{R}_0, \mathbf{r}_1 \dots \mathbf{r}_n, \mathbf{P}_0, \mathbf{p}_1 \dots \mathbf{p}_n | \mathbf{R}') d\mathbf{P}_0 \quad (23)$$

Combining (22) with FDR (20) (which, of course, is valid at any density if equal on both sides), we obtain

$$V_0(t, \Delta\mathbf{R}; \nu(\nu_0, \psi)) = V_0(t, \Delta\mathbf{R}; \nu_0) + \sum_{n=1}^{\infty} \frac{\phi^n}{n!} V_n(t, \Delta\mathbf{R}; \nu_0), \quad (24)$$

where now $\Delta\mathbf{R} \equiv \mathbf{R}_0 - \mathbf{R}'$.

Relation (24) thoroughly may be qualified as “virial expansion” of the BP’s path probability distribution, $V_0(t, \Delta\mathbf{R}; \nu)$, similarly to well-known virial expansions of thermodynamical quantities [24] or kinetic coefficients [9]. But there is significant mathematical difference between them: the two latter expand over absolute value of density ν while the former in fact over its relative value ν/ν_0 .

2.6. First-order relations

First-order, in respect to ϕ , terms of (24) produce

$$\tilde{\nu}_0 \frac{\partial V_0(t, \Delta \mathbf{R}; \nu_0)}{\partial \nu_0} = V_1(t, \Delta \mathbf{R}; \nu_0) = \nu_0 \int_{r \times p} \int V_1(t, \mathbf{R}_0, \mathbf{P}_0, \mathbf{r}_1, \mathbf{p}_1 | \mathbf{R}') d\mathbf{P}_0 \quad (25)$$

Here $\Delta \mathbf{R} = \mathbf{R}_0 - \mathbf{R}'$ and, according to (17) and/or (21),

$$\tilde{\nu}_0 \equiv \left[\frac{\partial \nu(\nu_0, \psi)}{\partial \psi} \right]_{\psi=0} = \nu_0 + \nu_0^2 \int [F_2^{(eq)}(\mathbf{r}) - 1] d\mathbf{r} = \nu_0 T \left(\frac{\partial \nu_0}{\partial P} \right)_T \quad (26)$$

Here, of course, $F_2^{(eq)}(\mathbf{r})$ is some function of ν_0 . The last equality in (26), with P standing for the pressure and the bracket representing compressibility, is well known from statistical thermodynamics [24].

Notice that the function $V_1(t, \Delta \mathbf{R}; \nu_0)$ can be interpreted as total pair correlation of BP with whole gas but counted per (elementary volume ν_0^{-1} what falls at) one gas atom. Similar interpretation is applicable to higher-order integral correlations (23).

Returning to our basic relation (18) in the full phase space, in the first order with respect to ψ we have

$$\begin{aligned} \left[\frac{\delta V\{t, \mathbf{R}' | \psi, \mathbf{R}_0, \mathbf{P}_0\}}{\delta \psi(\mathbf{r}, \mathbf{p})} \right]_{\psi=0} G_M(\mathbf{P}_0) e^{-\mathbf{f} \cdot [\mathbf{R}' - \mathbf{R}_0]/T} = \\ = \nu_0 V_1(t, \mathbf{R}_0, \mathbf{r}, -\mathbf{P}_0, -\mathbf{p} | \mathbf{R}') \end{aligned} \quad (27)$$

With the help of (17), variational derivative with respect to ψ can be replaced by that with respect to density of atoms in μ -space:

$$\begin{aligned} \left[\frac{\delta V}{\delta \psi(\mathbf{r}, \mathbf{p})} \right]_{\psi=0} = \nu_0 G_m(\mathbf{p}) F_1^{(eq)}(\mathbf{r} | \mathbf{R}_0) \frac{\delta V}{\delta \mu(\mathbf{r}, \mathbf{p})} + \nu_0^2 G_m(\mathbf{p}) \times \\ \times \int \int G_m(\mathbf{p}') [F_2^{(eq)}(\mathbf{r}, \mathbf{r}' | \mathbf{R}_0) - F_1^{(eq)}(\mathbf{r} | \mathbf{R}_0) F_1^{(eq)}(\mathbf{r}' | \mathbf{R}_0)] \frac{\delta V}{\delta \mu(\mathbf{r}', \mathbf{p}')} d\mathbf{r}' d\mathbf{p}' \end{aligned} \quad (28)$$

with the right-hand variational derivatives taken at $\mu(\mathbf{r}, \mathbf{p}) = \nu_0 G_m(\mathbf{p}) F_1^{(eq)}(\mathbf{r} | \mathbf{R}_0)$, i.e. at equilibrium gas with the seed density ν_0 . This generalizes (26) to arbitrary non-uniform perturbations.

The two latter formulas establish quite rigorous connection of, from one hand, pair correlation between previous path of BP and current state of the medium where it is walking, and, from the other hand, linear susceptibility of the BP's path probability distribution to weak perturbations of the medium.

3. Ranges of spatial statistical correlations between medium and Brownian particle and restrictions on its path probability distribution

Our previous results clearly show that, firstly, historical correlations between BP and medium (gas or liquid) certainly exist, i.e. are not zeros. Secondly, their total values (integrated over all momenta and relative distances between atoms and BP as in (23)) quite definitely reflect sensitivity of the probabilistic law of Brownian motion to change of state of the medium, first of all, to density of its atoms.

Indeed, let the medium represents three-dimensional weakly non-ideal ("dilute") gas in equilibrium ($\mathbf{f} = 0$). Then, undoubtedly, an increase of gas density must lead to constriction of the distribution $V_0(t, \Delta \mathbf{R}; \nu)$. Thus its density derivative

$\partial V_0(t, \Delta \mathbf{R}; \nu_0)/\partial \nu_0$ is positive at sufficiently small $|\Delta \mathbf{R}|$ but negative at relatively large $|\Delta \mathbf{R}|$. Since, undoubtedly again, auto-correlation of BP's velocity is integrable and therefore BP's chaotic walk is organized as "diffusion" considered already in [1, 2], i.e. $\Delta \mathbf{R}^2(t) \propto Dt$, $\int \Delta \mathbf{R}^2 V_0(t, \Delta \mathbf{R}; \nu_0) d\Delta \mathbf{R} = 6Dt$, a bound what separates "small" and "large" values of $|\Delta \mathbf{R}|$ is of order of $2\sqrt{Dt}$. Hence, we can state that $\partial V_0(t, \Delta \mathbf{R}; \nu_0)/\partial \nu_0 < 0$ when $z \equiv \Delta \mathbf{R}^2/4Dt$ is significantly greater than unit.

This implies, according to (25), that total pair BP-gas correlation, $V_1(t, \Delta \mathbf{R}; \nu_0)$, also is negative at large z , and thus $V_1(t, \mathbf{R}_0, \mathbf{P}_0, \mathbf{r}_1, \mathbf{p}_1 | \mathbf{R}')$ somewhere is negative. But it can not be "too negative", because its contribution to right side of (13) should not make its left side (which represents probability distribution) negative. This means, obviously, that the integral $V_1(t, \Delta \mathbf{R}; \nu_0)$ and thus the derivative $\nu_0 \partial V_0(t, \Delta \mathbf{R}; \nu_0)/\partial \nu_0$ is bounded below by some negative whose absolute value is proportional to $V_0(t, \Delta \mathbf{R}; \nu_0)$. Such restriction of the derivative, in its turn, means that tails of $V_0(t, \Delta \mathbf{R}; \nu_0)$ at $z \gg 1$ can not decrease in too fast way. Anyhow, possibility of exponential decrease of $V_0(t, \Delta \mathbf{R}; \nu_0)$ at $z \gg 1$ and hence the Gaussian asymptotic (1) become under question. Let us consider this suspicion carefully.

3.1. Restriction on the BP's path distribution tails. Estimate 1

At any t , \mathbf{R}' , \mathbf{R}_0 , \mathbf{P}_0 and \mathbf{p} , let

$$h(t, \mathbf{R}_0 - \mathbf{R}', \mathbf{P}_0, \mathbf{p}) = \min_{\mathbf{r}} V_1(t, \mathbf{R}_0, \mathbf{r}, \mathbf{P}_0, \mathbf{p} | \mathbf{R}')$$

Assume that at given t , \mathbf{R}' , \mathbf{R}_0 , \mathbf{P}_0 and \mathbf{p} integral of $V_1(t, \mathbf{R}_0, \mathbf{r}, \mathbf{P}_0, \mathbf{p} | \mathbf{R}')$ over \mathbf{r} is negative (i.e. $V_1(t, \Delta \mathbf{R}; \nu_0) < 0$). This means that $h(t, \mathbf{R}_0 - \mathbf{R}', \mathbf{P}_0, \mathbf{p})$ also is negative, and therefore we can introduce effective volume occupied by negative pair correlation, $\Omega_{neg}(t, \Delta \mathbf{R}, \mathbf{P}_0, \mathbf{p})$, by means of

$$\Omega_{neg}(t, \Delta \mathbf{R}, \mathbf{P}_0, \mathbf{p}) \equiv \frac{\int V_1(t, \mathbf{R}_0, \mathbf{P}_0, \mathbf{r}, \mathbf{p} | \mathbf{R}') d\mathbf{r}}{h(t, \Delta \mathbf{R}, \mathbf{P}_0, \mathbf{p})} \quad (29)$$

Clearly, this is lower boundary of volumes what could be reasonably attributed to the negative correlation. If, in opposite, the integral over \mathbf{r} is positive, in the same sense it is reasonable to assign $\Omega_{neg}(t, \Delta \mathbf{R}, \mathbf{P}_0, \mathbf{p}) = 0$. Then in any case we can write

$$\int V_1(t, \mathbf{R}_0, \mathbf{P}_0, \mathbf{r}, \mathbf{p} | \mathbf{R}') d\mathbf{r} \geq \Omega_{neg}(t, \Delta \mathbf{R}, \mathbf{P}_0, \mathbf{p}) h(t, \Delta \mathbf{R}, \mathbf{P}_0, \mathbf{p}) \quad (30)$$

Next, pay our attention to identity (13). Since the pair DF F_1 represents a probability density, it must be non-negative, $F_1(t, \mathbf{R}_0, \mathbf{r}, \mathbf{P}_0, \mathbf{p} | \mathbf{R}') \geq 0$. Hence,

$$h(t, \Delta \mathbf{R}, \mathbf{P}_0, \mathbf{p}) \geq -V_0(t, \mathbf{R}_0, \mathbf{P}_0 | \mathbf{R}') G_m(\mathbf{p}) \max F_1^{(eq)} \quad (31)$$

with $\max F_1^{(eq)}$ denoting maximum of all values of $F_1^{(eq)}(\mathbf{r} | \mathbf{R}_0)$ at those points \mathbf{r} where $V_1(t, \mathbf{R}_0, \mathbf{r}, \mathbf{P}_0, \mathbf{p} | \mathbf{R}')$ takes its minimum value $h(t, \mathbf{R}_0 - \mathbf{R}', \mathbf{P}_0, \mathbf{p})$. This inequality will be even more so valid if replace $\max F_1^{(eq)}$ by absolute maximum of F_1 : $\max F_1^{(eq)} \rightarrow \max_{\mathbf{r}} F_1^{(eq)}(\mathbf{r} | \mathbf{R}_0)$.

It is useful to notice that $F_1(t, \mathbf{R}_0, \mathbf{r} = \mathbf{R}_0, \mathbf{P}_0, \mathbf{p} | \mathbf{R}') = 0$, $F_1^{(eq)}(\mathbf{R}_0 | \mathbf{R}_0) = 0$ and therefore $V_1(t, \mathbf{R}_0, \mathbf{r} = \mathbf{R}_0, \mathbf{P}_0, \mathbf{p} | \mathbf{R}') = 0$, if BP and an atom can not be located at same point. Consequently, always $h(t, \Delta \mathbf{R}, \mathbf{P}_0, \mathbf{p}) \leq 0$.

Combining inequalities (30) and (31) and relation (25), we come to inequality

$$\begin{aligned} \tilde{\nu}_0 \frac{\partial V_0(t, \Delta \mathbf{R}; \nu_0)}{\partial \nu_0} &\geq -\nu_0 \max F_1^{(eq)} \times \\ &\times \int \int \Omega_{neg}(t, \Delta \mathbf{R}, \mathbf{P}_0, \mathbf{p}) V_0(t, \mathbf{R}_0, \mathbf{P}_0 | \mathbf{R}') G_m(\mathbf{p}) d\mathbf{p} d\mathbf{P}_0 \end{aligned} \quad (32)$$

It remains to uncouple the joint distribution of BP's path and momentum:

$$V_0(t, \mathbf{R}_0, \mathbf{P}_0 | \mathbf{R}') = V_0(t, \Delta \mathbf{R}; \nu_0) G(t, \mathbf{P}_0 | \Delta \mathbf{R}) ,$$

where last multiplier is conditional probability distribution of the momentum under given path value, and introduce conditional average correlation volume

$$\bar{\Omega}_{neg}(t, \Delta \mathbf{R}) = \int \int \Omega_{neg}(t, \Delta \mathbf{R}, \mathbf{P}_0, \mathbf{p}) G(t, \mathbf{P}_0 | \Delta \mathbf{R}) G_m(\mathbf{p}) d\mathbf{p} d\mathbf{P}_0 \quad (33)$$

After that inequality (32) takes the form

$$\tilde{\nu}_0 \frac{\partial V_0(t, \Delta \mathbf{R}; \nu_0)}{\partial \nu_0} + \nu_0 \max F_1^{(eq)} \bar{\Omega}_{neg}(t, \Delta \mathbf{R}) V_0(t, \Delta \mathbf{R}; \nu_0) \geq 0 \quad (34)$$

of declared restriction on rate of change of $V_0(t, \Delta \mathbf{R})$. Before discussing it, consider another variant of the restriction [14].

3.2. Restriction on the BP's path distribution tails. Estimate 2

Let Ω denotes at once a finite region in the \mathbf{r} -space and volume of this region, presuming that it is centered near point \mathbf{R}_0 . Introduce $\Omega(\delta) = \Omega(t, \Delta \mathbf{R}, \mathbf{P}_0, \mathbf{p}, \delta)$ as minimum of all those regions Ω what satisfy

$$\left| \int_{\Omega} V_1(t, \mathbf{R}_0, \mathbf{r}, \mathbf{P}_0, \mathbf{p} | \mathbf{R}') d\mathbf{r} - \int V_1(t, \mathbf{R}_0, \mathbf{r}, \mathbf{P}_0, \mathbf{p} | \mathbf{R}') d\mathbf{r} \right| < \delta \left| \int V_1(t, \mathbf{R}_0, \mathbf{r}, \mathbf{P}_0, \mathbf{p} | \mathbf{R}') d\mathbf{r} \right|$$

with some fixed $0 < \delta < 1$. That is $\Omega_{cor}(\delta)$ represents minimal region containing at least $100(1 - \delta)$ percents of the total pair correlation.

From the other hand, integrate identity (13) over $\mathbf{r}_1 \in \Omega(\delta)$. In view of the non-negativeness of $F_1(t, \mathbf{R}_0, \mathbf{r}_1, \mathbf{P}_0, \mathbf{p}_1 | \mathbf{R}')$ result must be non-negative:

$$\int_{\Omega(\delta)} F_1^{(eq)}(\mathbf{r} | \mathbf{R}_0) d\mathbf{r} V_0(t, \mathbf{R}_0, \mathbf{P}_0 | \mathbf{R}') G_m(\mathbf{p}) + \int_{\Omega(\delta)} V_1(t, \mathbf{R}_0, \mathbf{r}, \mathbf{P}_0, \mathbf{p} | \mathbf{R}') d\mathbf{r} \geq 0$$

It is easy to verify that these two inequalities together imply a more interesting one:

$$\begin{aligned} \int_{\Omega(\delta)} F_1^{(eq)}(\mathbf{r} | \mathbf{R}_0) d\mathbf{r} V_0(t, \mathbf{R}_0, \mathbf{P}_0 | \mathbf{R}') G_m(\mathbf{p}) + \\ + (1 - \delta) \int V_1(t, \mathbf{R}_0, \mathbf{r}, \mathbf{P}_0, \mathbf{p} | \mathbf{R}') d\mathbf{r} \geq 0 \end{aligned} \quad (35)$$

Next, again let us replace here $F_1^{(eq)}$ by $\max F_1^{(eq)}$ (which even improves the inequality), then perform integration over momentums, apply relation (25) and divide all by $(1 - \delta)$. This yields

$$\nu_0 \max F_1^{(eq)} \bar{\Omega}(t, \Delta \mathbf{R}, \delta) V_0(t, \Delta \mathbf{R}; \nu_0) + \tilde{\nu}_0 \frac{\partial V_0(t, \Delta \mathbf{R}; \nu_0)}{\partial \nu_0} \geq 0 \quad (36)$$

with characteristic average pair correlation volume defined by

$$\bar{\Omega}(t, \Delta \mathbf{R}, \delta) = (1 - \delta)^{-1} \int \int \Omega(t, \Delta \mathbf{R}, \mathbf{P}_0, \mathbf{p}, \delta) G(t, \mathbf{P}_0 | \Delta \mathbf{R}) G_m(\mathbf{p}) d\mathbf{p} d\mathbf{P}_0 \quad (37)$$

Unlike (33) this characteristic volume has free parameter $0 < \delta < 1$. At $\delta \ll 1$ almost all pair correlation is taken into account. But to make inequality (36) most strong we have to minimize $\bar{\Omega}(t, \Delta \mathbf{R}, \delta)$ with respect to δ . From this point of view, a choice when $1 - \delta \ll 1$ can be preferred. At that, expectedly, $\bar{\Omega}(t, \Delta \mathbf{R}, \delta)$ is close to above defined $\bar{\Omega}_{neg}(t, \Delta \mathbf{R})$ if total pair correlation is negative.

3.3. Finiteness of the correlation volume and failure of the Gaussian asymptotic

Let us consider equilibrium and hence spherically symmetric Brownian motion what takes place in absence of the external force ($\mathbf{f} = 0$). Assume that at sufficiently large scales, when $t \gg \tau$, with τ being BP's mean free-flight time, and

$$\langle \Delta \mathbf{R}^2(t) \rangle = \int \Delta \mathbf{R}^2 V_0(t, \Delta \mathbf{R}; \nu_0) d\Delta \mathbf{R} = 6Dt \gg 3\Lambda^2,$$

with Λ being BP's mean free path, the probability distribution of BP's path, $V_0(t, \Delta \mathbf{R}; \nu_0)$, tends to the Gaussian (1). Then it depends on gas density by way of the BP's diffusivity D only, and inequalities (34) or (36) produce, together with (26),

$$\left[c_1(t, \Delta \mathbf{R}) + \left(\frac{\Delta \mathbf{R}^2}{4Dt} - \frac{3}{2} \right) \left(\frac{\partial \ln D}{\partial \ln \nu_0} \right) T \left(\frac{\partial \nu_0}{\partial P} \right)_T \right] V_G(t, \Delta \mathbf{R}) \geq 0 \quad (38)$$

where, respectively,

$$c_1(t, \Delta \mathbf{R}) = \nu_0 \max F_1^{(eq)} \bar{\Omega}_{neg}(t, \Delta \mathbf{R}), \quad c_1(t, \Delta \mathbf{R}) = \nu_0 \max F_1^{(eq)} \bar{\Omega}(t, \Delta \mathbf{R}, \delta)$$

In case of gas, certainly, BP's diffusivity is a decreasing function of the density, $\partial \ln D / \partial \ln \nu_0 < 0$. Hence, the second addend in square bracket becomes negative at $z = \Delta \mathbf{R}^2 / 4Dt > 3/2$. As the consequence, inequality (38) can be satisfied if and only if at large values of z quantity $c_1(t, \Delta \mathbf{R})$ grows at least proportionally to z .

Notice that for not too dense gas (all the more, for dilute one) we can write $\Lambda = v_T \tau$ and $D \approx v_T \Lambda = v_T^2 \tau$, where $v_T \sim \sqrt{T/M}$ is characteristic thermal velocity of BP. Besides, for molecular-size BP (whose mass is comparable with atomic mass) $v_T \sim v_s$. This makes it obvious that limits of the quasi-uniform gas perturbation (see section 2.5) practically allows arbitrary large values of z , up to $z \sim v_s^2 t_0 / 4D \sim t_0 / \tau$, where t_0 is total duration of the “full-scale experiment”. Therefore inequality (38) requires from $c_1(t, \Delta \mathbf{R})$ and thus from $\nu_0 \bar{\Omega}$, with $\bar{\Omega}$ being minimum of (33) and (37), ability to achieve as large values as t_0 / τ (where t_0 , in its turn, is arbitrary large).

For dilute gas, more concretely, it is known that $\max F_1^{(eq)} = 1$, $T \partial \nu_0 / \partial P = 1$, and $\Lambda = (\pi r_B^2 \nu_0)^{-1} \propto 1/\nu_0$, where r_B is effective radius of BP-atom short-range repulsive interaction. Consequently, $\partial \ln D / \partial \ln \nu_0 = -1$, and (38) satisfies only when $\nu_0 \bar{\Omega} + 3/2 \geq z = \Delta \mathbf{R}^2 / 4Dt$ at any z .

In fact, **we are faced with dilemma: either asymptotical statistics of Brownian path is Gaussian or volume of pair correlation is bounded above.**

What is better? In the first variant, “the law of large numbers” and conventional stochastic picture of Brownian motion hold true. But the strange enough requirement of unrestrictedly wide spatial statistical correlations indicates presence of self-contradictions in such theory. In the second variant, “the law of large numbers” does not work. But there are no nonphysical requirements and no contradictions.

Undoubtedly, we have to prefer this second variant and claim that Brownian trajectory can not be imitated with the help of coin tossing or dice tossing or other “statistically independent” random events.

3.4. Volume of pair correlation (volume of collisions)

In order to make our consideration more pointed and *a fortiori* exclude from it any “collective” or “hydrodynamic” effects, a toy named “the Boltzmann-Grad limit” (BGL) is very useful. In this limit $\nu_0 \rightarrow \infty$ while $r_B \sim r_A \rightarrow 0$ (r_B and r_A are radii of short-range repulsive BP-atom and atom-atom interactions) in such way that gas non-ideality parameters $4\pi r_A^3 / 3$ and $4\pi r_B^3 / 3$ vanish but mean free paths of

of BP, $\Lambda = (\pi r_B^2 \nu_0)^{-1}$, and atoms, $\lambda = (\pi r_A^2 \nu_0)^{-1}$, stay fixed. At that, BP collides with only infinitely small portion of atoms what surround it, therefore its previous collisions in no way can influence next ones.

Folklore of kinetics includes opinion that at least under BGL the Boltzmann equation is true “zero-order approximation” for finite-density gas kinetics, and the corresponding Boltzmann-Lorentz equation (see e.g. [7]) for molecular BP (test atom or particle of rare impurity) is exact zero-order approximation for molecular Brownian motion. Since this equation inevitably yields [7, 16] the Gaussian asymptotic, a best chance to resolve above formulated dilemma in detail is to consider pair correlations in the course of the BGL. For simplicity, again at $\mathbf{f} = 0$.

Recall a few things about pair CF, $V_1(t, \mathbf{R}_0, \mathbf{r}, \mathbf{P}_0, \mathbf{p} | \mathbf{R}')$, already known from conventional theory [7, 5, 8]. In respect to relative distance between two particles (in our case, BP and an atom), $\mathbf{r} - \mathbf{R}_0$, the pair correlation is accumulated inside a “collision cylinder” which has radius $\approx r_B$ and is directed in parallel to relative velocity of the particles, $\mathbf{v} - \mathbf{V}_0 = \mathbf{p}/m - \mathbf{P}_0/M$. Importantly, characteristic value of the pair CF in this cylinder is comparable with product of one-particle DF. In our case this means that magnitude of $V_1(t, \mathbf{R}_0, \mathbf{r}, \mathbf{P}_0, \mathbf{p} | \mathbf{R}')$ (in particular, above defined quantity $h(t, \Delta \mathbf{R}, \mathbf{P}_0, \mathbf{p})$) is of order of first right-hand term in (13). As the consequence, magnitude of pair correlation, as well as $V_0(t, \mathbf{R}_0, \mathbf{P}_0 | \mathbf{R}')$, keeps safe under BGL, although inside more and more narrow *collision cylinder* only.

But what is spread of pair correlation along the cylinder? Unfortunately, conventional theory never was interested in this issue, but in fact it reserves the spread to be infinite, at least at $(\mathbf{v} - \mathbf{V}_0) \cdot (\mathbf{r} - \mathbf{R}_0) > 0$, i.e. for particles flying away after collision. As the consequence, integral $\int V_1(t, \mathbf{R}_0, \mathbf{r}, \mathbf{P}_0, \mathbf{p} | \mathbf{R}') d\mathbf{r}$, integral in (25) and corresponding correlation volumes all turn to infinity.

This became possible since the theory [7, 5, 8] neglected contributions from three-particle and other higher-order correlations, V_2 , V_3 , etc., although they involve collisions of the pair under attention with “third particles” (the rest of gas). That are not literally three-particle collisions but chains of (actual or virtual) pair collisions [10, 11, 16]. It is not too hard to look after that magnitude of n -order CF on corresponding sets in n -particle phase spaces at $n = 3, \dots$, like at $n = 2$, is of order of product of n one-particles DF irrespective to BGL. Therefore, due to collisions with “third particles”, the pair correlation of BP with atoms disappears when $|\mathbf{r} - \mathbf{R}_0|$ significantly exceeds Λ . Stronger separated particles hardly are participants of forthcoming or happening mutual collision, even if they aim precisely one to another.

By neglecting all that, the theory unknowingly resolves the dilemma in favor of its first variant. That is why conventional kinetics, including the Boltzmann equation, is not true “zero-order approximation” and contradicts the virial relations.

In fact, according to above remarks, a spread of the pair correlation along collision cylinder is finite and characterized by minimum of mean free paths Λ and λ . Correspondingly, effective volume of the cylinder, or volume of pair correlation, $\bar{\Omega}$, is finite value of order of $\pi r_B^2 \Lambda = \nu_0^{-1}$ (assuming, for simplicity, $\lambda \sim \Lambda$), i.e. volume displayed per one atom. Since our reasonings are irrespective to where and when pair collisions take place, the estimate $\bar{\Omega} \sim \pi r_B^2 \Lambda = \nu_0^{-1}$ is independent on t and $\Delta \mathbf{R}$ and at once is estimate of upper boundary of the correlation volume.

Let us consider this conclusion from the point of view of virial relations (18), (22) with (23), (24), (25) and (27) with (28).

3.5. God does not play dice with the Boltzmann-Grad gas

It is easy to make sure that on the way to BGL, at any fixed function $\phi(\mathbf{r})$, expressions (17), (21) and (26) simplify to

$$\begin{aligned} \frac{\nu\{\mathbf{r}|\phi, \mathbf{R}_0\}}{\nu_0} &\rightarrow 1 + \phi(\mathbf{r}) , & \frac{\nu(\nu_0, \phi)}{\nu_0} &\rightarrow 1 + \phi , & \frac{\tilde{\nu}_0}{\nu_0} &\rightarrow 1 , \\ \frac{\mu\{\mathbf{r}, \mathbf{p}|\psi, \mathbf{R}_0\}}{\nu_0} &\rightarrow [1 + \psi(\mathbf{r}, \mathbf{p})] G_m(\mathbf{p}) \end{aligned} \quad (39)$$

Since change of ν_0 during BGL is compensated by change of r_B and r_A to keep constant Λ and λ , left sides of (18), (22), (24) and (25) become invariants of ν_0 although keeping their dependence on ϕ . Consequently, all coefficients in right-hand expansions into power series of ϕ become independent on ν_0 . On the left, the expansion means application of operators $(\partial/\partial\phi)^n$ which is equivalent to action of operators $\nu_0^n [\partial/\partial\nu_0]^n$ at fixed r_B and r_A . Then under BGL any result of this operation also is independent on ν_0 .

What is for relations (27) and (28), they turn to

$$G_m(\mathbf{p})G_M(\mathbf{P}_0) \frac{\delta V\{t, \mathbf{R}'|\psi, \mathbf{R}_0, \mathbf{P}_0\}}{\delta\mu(\mathbf{r}, \mathbf{p})} e^{-\mathbf{r}\cdot[\mathbf{R}' - \mathbf{R}_0]/T} = V_1(t, \mathbf{R}_0, \mathbf{r}, -\mathbf{P}_0, -\mathbf{p}|\mathbf{R}') \quad (40)$$

with variational derivative taken at $\mu(\mathbf{r}, \mathbf{p}) = \nu_0 G_m(\mathbf{p})$. Obviously, this derivative represents reaction of probability distribution of BP's path, $\mathbf{R}' - \mathbf{R}_0$, to lodging, at $t = 0$, in point \mathbf{r} one extra atom with momentum \mathbf{p} . At that, importantly, it is presumed that this extra atom does not disturb initial equilibrium (of the statistical ensemble), as if it was merely marked atom.

Far enough under BGL, of course, this lodging can have an effect at such initial relative disposition of BP and the extra atom only which results in their direct collision. Hence, vector $\mathbf{r} - \mathbf{R}_0$ should belong to those part of the *collision cylinder* which corresponds either to particles in *in*-state, i.e. flying one towards another, or to currently colliding (interacting) particles, i.e. separated by distance $|\mathbf{r} - \mathbf{R}_0| \lesssim r_B$.

Besides, $|\mathbf{r} - \mathbf{R}_0|$ should not be much greater than $\min(\Lambda, \lambda)$. Otherwise collisions of either BP or extra atom with "third particles" (other atoms) will prevent the desired collision. This trivial notation once again, but more strikingly, highlights that volume occupied by the pair correlation on right-hand side of (40) can be estimated (at $\lambda \sim \Lambda$) as $\bar{\Omega} \sim \pi r_B^2 \Lambda = \nu_0^{-1}$ irrespective to the BP's path. Indeed, on the left in (40), in view of the causality principle, a whole future path of BP can not influence possibility of its collision with concrete marked atom at very beginning of the path. Moreover, the mentioned path and collision can not be mutually statistically correlated since the marked atom and BP deal with different non-intercrossing collections of "third particles". Therefore, any dependence of the right-hand pair CF on t and $\Delta\mathbf{R}$ characterizes its magnitude but not its spread.

Now we can say almost with confidence, that correlation volumes $\bar{\Omega}_{neg}(t, \Delta\mathbf{R})$, $\Omega(t, \Delta\mathbf{R}, \mathbf{P}_0, \mathbf{p}, \delta) = \Omega(\delta)$ and $\bar{\Omega}(t, \Delta\mathbf{R}, \delta)$, introduced in sections 3.1 and 3.2, have upper boundary $\sim \nu_0^{-1}$ independent on t and $\Delta\mathbf{R}$ or z , and should be written simply as $\bar{\Omega}_{neg}$, $\Omega(\mathbf{P}_0, \mathbf{p}, \delta) = \Omega(\delta)$ and $\bar{\Omega}(\delta)$. Correspondingly, $c_1(t, \Delta\mathbf{R})$ in (38) is not a function but a constant of order of unit.

Thus, the second resolution of the dilemma from section 3.3 is acceptable only. We can say that the god of mechanics does not play dice. He disposes of stronger means: Hamiltonian dynamics of many particles ($N > t_0/\tau$, according to [13, 14, 16]) is able to create much more rich randomness than dice tossing can do.

3.6. Probability distribution of BP's path possesses power-law long tails

Now we are ready to discuss what kind of asymptotic of BP's path distribution is really allowed instead of the Gaussian one.

According to previous section, let us rewrite inequalities (34) or (36) in the form

$$c_1 V_0(t, \Delta \mathbf{R}; \nu_0) + \tilde{\nu}_0 \frac{\partial V_0(t, \Delta \mathbf{R}; \nu_0)}{\partial \nu_0} \geq 0, \quad (41)$$

Here c_1 is a constant whose upper estimates obtained in two different ways look as

$$c_1 = \nu_0 \max F_1^{(eq)} \bar{\Omega}_{neg}, \quad c_1 = \nu_0 \max F_1^{(eq)} \bar{\Omega}(\delta)$$

with $\bar{\Omega}_{neg}$ and $\bar{\Omega}(\delta)$ being volumes of pair correlation (volumes of collision) defined by (33) and (37) and bounded above by a value $\sim \nu_0^{-1}$ (volume per one atom), so that $c_1 \sim 1$. Probably, there are methods to estimate c_1 differently from sections 3.1 and 3.2. Anyway, to make inequality (41) stronger, we should take minimum of all available estimates.

For simplicity, consider equilibrium Brownian motion at $\mathbf{f} = 0$. In case of dilute enough gas, or even liquid in three or more dimensions, when hydrodynamical contributions to BP's velocity are far from domination, and the "diffusion law" $\Delta \mathbf{R}^2 \propto t$ holds, it seems natural if asymptotically, at $t \gg \tau$, the BP's path distribution $V_0(t, \Delta \mathbf{R}; \nu_0)$ is characterized, similarly to $V_G(t, \Delta \mathbf{R})$, by a single parameter, that is diffusivity. For 3-D space,

$$V_0(t, \Delta \mathbf{R}; \nu_0) \rightarrow (4Dt)^{-3/2} \Psi(\Delta \mathbf{R}^2/4Dt) \quad (42)$$

Here it is presumed that

$$\int \Psi(\mathbf{a}^2) d\mathbf{a} = 1, \quad \int \mathbf{a}^2 \Psi(\mathbf{a}^2) d\mathbf{a} = 3/2 \quad (43)$$

The first of these requirements is the normalization condition, while the second means that $\langle \Delta \mathbf{R}^2(t) \rangle = 6Dt$ and in fact serves as quantitative definition of the diffusivity. Then, inequality (41) yields

$$\alpha \Psi(z) + z \frac{d\Psi(z)}{dz} \geq 0, \quad \alpha \equiv \frac{3}{2} + c_1 \left| \frac{\tilde{\nu}_0}{D} \frac{\partial D}{\partial \nu_0} \right|^{-1}, \quad (44)$$

if diffusivity is a decreasing function of density, $\partial D/\partial \nu_0 < 0$, and

$$\alpha \Psi(z) + z \frac{d\Psi(z)}{dz} \leq 0, \quad \alpha \equiv \frac{3}{2} - c_1 \left| \frac{\tilde{\nu}_0}{D} \frac{\partial D}{\partial \nu_0} \right|^{-1}$$

in opposite case $\partial D/\partial \nu_0 > 0$.

Confining ourselves by the first case, we see that function $\Psi(z)$ must have power-law long tail: $\Psi(z) \propto z^{-\beta}$ at $z \rightarrow \infty$, where $\beta \leq \alpha$. At that, in order to satisfy second of conditions (43), exponent α should be greater than 5/2.

Example of such behavior, with maximally possible $\beta = \alpha$, is presented by

$$\Psi(z) = \frac{\gamma(\alpha)}{(1+z)^\alpha}, \quad V_0(t, \Delta \mathbf{R}; \nu_0) \rightarrow \frac{\gamma(\alpha)}{(4D't)^{3/2}} \left(1 + \frac{\Delta \mathbf{R}^2}{4D't}\right)^{-\alpha}, \quad (45)$$

where $\gamma(\alpha) = \pi^{-3/2} \Gamma(\alpha)/\Gamma(\alpha - 3/2)$ and $D' = (\alpha - 5/2)D$.

Unpleasant aspect of such behavior is unboundedness of high enough statistical moments of $\Delta \mathbf{R}$. However, recall that real Brownian motion in addition to diffusivity has at least one more important parameter, namely, the BP's thermal velocity v_T .

Then $V_0(t, \Delta \mathbf{R})$ should be considered as a function of two dimensionless parameters, $z = \Delta \mathbf{R}^2/4Dt$ and $y = \mathbf{R}^2/v_T^2 t^2$, and asymptotically instead of (44) we can write

$$V_0(t, \Delta \mathbf{R}) \rightarrow \frac{1}{(4Dt)^{3/2}} \Phi\left(\frac{\Delta \mathbf{R}^2}{4Dt}, \frac{\Delta \mathbf{R}^2}{v_T^2 t^2}\right) \rightarrow \frac{1}{(4Dt)^{3/2}} \Psi\left(\frac{\Delta \mathbf{R}^2}{4Dt}\right) \Theta\left(\frac{\Delta \mathbf{R}^2}{v_T^2 t^2}\right) \quad (46)$$

Here $\Psi(z)$ as before satisfies (43), while function $\Theta(y) \approx 1$ at $y \ll 1$ and fast enough tends to zero at $y > 1$ thus sharply cutting $V_0(t, \Delta \mathbf{R})$ when $|\mathbf{R}| > v_T t$. This variant also is allowed by inequality (41), because v_T is independent on density. And now all statistical moments of BP's are finite.

Nevertheless, from the point of view of higher-order moments, such asymptotic still is not exhaustive, excepting case of dilute gas. For sufficiently dense gas (all the more, liquid) we should take into account, at the minimum, such third (density-dependent) parameter as isothermal speed of sound, $v_s = \sqrt{T\nu_0/m\tilde{\nu}_0}$, with $\tilde{\nu}_0$ presented by (26). At the same time, such complications practically do not change main probabilistic characteristics of BP's path, as well as its mean square behavior, and in no case cancel the long power-law tails.

3.7. Comparison with solutions of the BBGKY equations

Previous results, obtained from the first-order virial relations (one- and two-particle CF) only, are in remarkable qualitative (and even semi-quantitative) agreement with results obtained in [16] from infinite chain of roughened BBGKY equations describing a test (marked) gas atom in the role of BP in the Boltzmann-Grad gas. But, of course, our approach here could not give numeric value of exponent α in (44) and (45). Approximate analysis in [16] gave distribution (2), that is $\alpha = 7/2$, which corresponds to $c_1 = \nu_0 \bar{\Omega} = 2$.

More precisely, solution obtained in [16] indeed has the form (46). At that, the cut-off function Θ works already at fourth-order statistical moment, yielding

$$\langle \Delta \mathbf{R}^4(t) \rangle = \int \Delta \mathbf{R}^4 V_0(t, \Delta \mathbf{R}) d\Delta \mathbf{R} \rightarrow 3 \langle \Delta \mathbf{R}^2(t) \rangle^2 \ln \frac{t}{\tau} \quad (47)$$

with $\langle \Delta \mathbf{R}^2(t) \rangle = 6Dt$. This result looks as if BP's diffusivity was fluctuating quantity, \tilde{D} , with mean $\langle \tilde{D} \rangle = D$ and variance $\langle \tilde{D}^2 \rangle - \langle \tilde{D} \rangle^2 \approx D^2 \ln(t/\tau)$ which depends on total duration of BP observation, t .

From the point of view of (2) variance of the fluctuating diffusivity, \tilde{D} , is infinite. But probability distribution of \tilde{D} is quite certain. One uncovers it representing (2) as superposition of Gaussians with various values of diffusivity:

$$V_0(t, \Delta \mathbf{R}) \rightarrow \frac{\Gamma(7/2)}{(4\pi Dt)^{3/2}} \left[1 + \frac{\Delta \mathbf{R}^2}{4Dt}\right]^{-7/2} = \int \frac{1}{(4\pi \zeta Dt)^{3/2}} \exp\left[-\frac{\Delta \mathbf{R}^2}{4\zeta Dt}\right] w(\zeta) d\zeta, \quad (48)$$

$$w(\zeta) = \frac{1}{\zeta^3} \exp\left(-\frac{1}{\zeta}\right),$$

where ζ represents \tilde{D}/D while $w(\zeta)$ is probability density of ζ .

At one and the same D distribution (2) or (48) seems rather dissimilar to the Gaussian (1). But in fact the only essential difference between them is long tail of (2). To make this visible, we may rescale (2) by suitable increase ("renormalization") of its diffusivity and compare one-dimensional projections of (1) and (2) onto some axis X . Left plot on Figure 1 illustrates such comparison, with rescaling factor $3\sqrt{\pi}/4$ which equalizes heights of both distributions at $X = 0$.

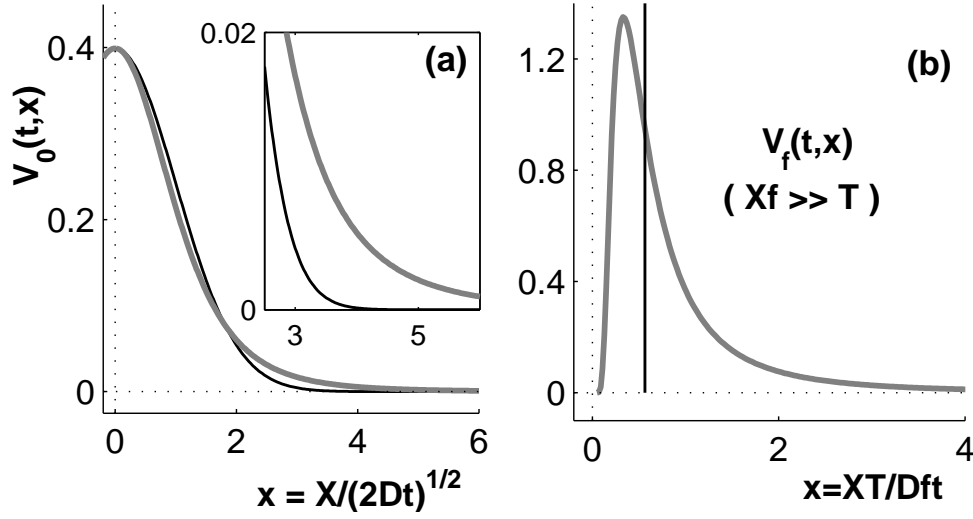


Figure 1. (a) Projections onto X -axis of reduced Gaussian distribution (1), $(2\pi)^{-1/2} \exp(-x^2/2)$ (thin black curve), and reduced rescaled non-Gaussian distribution (2), $(2\pi)^{-1/2}(1+8x^2/9\pi)^{-5/2}$ (thick gray curve); the inset magnifies tails of the distributions. (b) Reduced distribution (51), $x^{-3} \exp(-1/x)$ (thick gray curve), of drift displacement in comparison with reduced rescaled result, $\delta(x - 16/9\pi)$ (black vertical line), of usual theory.

Although in [16] only thermodynamically equilibrium Brownian motion was considered, the integral representation (48), as combined with FDR (20), can be used to predict statistics of non-equilibrium Brownian motion at $\mathbf{f} \neq 0$. Reasonableness of such operation, for a weak non-equilibrium, was confirmed e.g. in [21, 23]. The word “weak” means that BP’s drift velocity \mathbf{v}_d is much smaller than v_T and v_s and therefore is linear function of the external force:

$$\langle \Delta \mathbf{R}(t) \rangle = \int \Delta \mathbf{R} V_0(t, \Delta \mathbf{R}) d\Delta \mathbf{R} = \mathbf{v}_d t, \quad \mathbf{v}_d = D\mathbf{f}/T$$

Here D/T is mobility of BP, in agreement with the Einstein relation [1, 2] which, by the way, directly follows from (19) or (20) (see also [11, 19, 22]).

To underline dependence of $V_0(t, \Delta \mathbf{R})$ on the external force, let us denote it as $V_f(t, \Delta \mathbf{R})$. Then, if we do not wish to look on so far distances as $v_T t$ (all the more, $|\mathbf{f}|t^2/2M$), we can find asymptotic of $V_f(t, \Delta \mathbf{R})$ at $t \gg \tau$ in the form (48) but replacing equilibrium Gaussian components by non-equilibrium ones:

$$V_f(t, \Delta \mathbf{R}) \rightarrow \int \frac{1}{(4\pi\zeta Dt)^{3/2}} \exp\left[-\frac{(\Delta \mathbf{R} - \zeta D\mathbf{f}t/T)^2}{4\zeta Dt}\right] w(\zeta) d\zeta \quad (49)$$

Recollecting that $\partial \ln D / \partial \ln \nu_0 = -1$ under BGL, it is easy to make sure that this expression satisfies inequality (41), that is

$$c_1 V_f(t, \Delta \mathbf{R}) - D \frac{\partial V_f(t, \Delta \mathbf{R})}{\partial D} \geq 0, \quad c_1 = 2,$$

as well as equality (20). In short, (49) agrees with both virial relations and FDR.

Consider (49) at a time when drift of BP exceeds its diffusion, $|\mathbf{v}_d|t > \sqrt{6Dt}$. In other words, when $\mathbf{f} \cdot \mathbf{v}_d t \gg T$, i.e. work of the force much exceeds thermal energy per degree of freedom. At that, distribution $V_f(t, \Delta \mathbf{R})$ becomes highly asymmetric and

anisotropic. Therefore we have to distinguish BP's displacement X along direction of the force \mathbf{f} and two orthogonal displacements Y and Z . In such notations $\Delta\mathbf{R} = \{X, Y, Z\}$, and (49) yields

$$V_f(t, \{X, Y, Z\}) \rightarrow \frac{|\mathbf{f}|}{4\pi T X} \exp\left[-\frac{|\mathbf{f}|(Y^2 + Z^2)}{4TX}\right] \cdot \frac{\mathbf{v}_d^2 t^2}{X^3} \exp\left(-\frac{|\mathbf{v}_d|t}{X}\right) \quad (50)$$

At any fixed Y and Z this expression has long tail in positive X -direction, so that

$$V_f(t, X) \equiv \int \int V_f(t, \{X, Y, Z\}) dY dZ = \frac{\mathbf{v}_d^2 t^2}{X^3} \exp\left(-\frac{|\mathbf{v}_d|t}{X}\right), \quad (51)$$

but in strictly this direction only. Right-hand part of Figure 1 shows this asymptotical distribution of BP's drift, in comparison with drift distribution in conventional kinetics, which is nothing but delta-function $\delta(X - |\mathbf{v}_d|t)$. At the same time,

$\int V_f(t, \{X, Y, Z\}) dX = \int V_0(t, \{X, Y, Z\}) dX = (2\pi Dt)^{-1} [1 + (Y^2 + Z^2)/4Dt]^{-3}$ has long tail in any direction in YZ -plane, and anybody who keeps under observation Y and Z only sees no signs of BP's drift along X -axis.

Basic idea of [16], earlier suggested in [10, 11]), was to consider DF averaged over "collision boxes". The latter are just sets in n -particle phase spaces already mentioned in section 3.4. For $n = 2$, "collision box" is nothing but above exploited "collision cylinder". In general, "collision box" is a "skeleton" set of n -particle configurations snapped up from chains of $n - 1$ connected (actual or virtual) collisions, under given input momenta. Thorough description of all these sets hardly is possible, but hardly it is obligatory. Much more important thing is that even under rough description one immediately discovers that the Boltzmann-Grad gas is true *terra incognita*.

3.8. Origin of the historical correlations and long tails and $1/f$ noise

Let us return to identity (40). One and the same vector $\mathbf{r} - \mathbf{R}_0$ on its opposite sides belongs to opposite half of the *collision cylinder*. Hence, pair correlations on right-hand side are concentrated at *out*-states (i.e. concern particles flying away one from another) and at central region of the cylinder (i.e. concern also currently interacting particles, with $|\mathbf{r} - \mathbf{R}_0| \lesssim r_B$), while *in*-states are uncorrelated.

This consequence of (40) is in agreement with usual theory [5, 6, 7, 8]. The latter considers it as a good reason to believe in "statistical independency" of colliding particles (Boltzmann's "molecular chaos"). In present theory, however, actually colliding particles occupy central part of collision cylinder where, according to (40), $V_1(t, \mathbf{R}_0, \mathbf{r}, \mathbf{P}_0, \mathbf{p}|\mathbf{R}')$ is non-zero, and thus these particles are mutually correlated and statistically dependent. Hence, statistical dependency is not "exported from outside" but occurs at the time of collision.

The point is that $V_1(t, \mathbf{R}_0, \mathbf{r}, \mathbf{P}_0, \mathbf{p}|\mathbf{R}')$ (as well as higher-order CF) represents "historical correlations" (see section 2.3): it treats current collision as not a separate event but last term of long random sequence of BP's collisions with atoms on its way from \mathbf{R}' to \mathbf{R}_0 . Therefore statistical dependencies involved by $V_1(t, \mathbf{R}_0, \mathbf{r}, \mathbf{P}_0, \mathbf{p}|\mathbf{R}')$ should be addressed not to currently colliding particles (BP and atom) themselves but to long-range fluctuations in relative frequency of BP's collisions.

With the purpose to make certain that this is only reasonable understanding of the correlations, in particular spatial ones, $V_n(t, \Delta\mathbf{R}; \nu_0)$ ($n \geq 1$), let us introduce, in terms of section 3.2, function

$$W_1(t, \Delta\mathbf{R}) = \frac{\nu_0}{1 - \delta} \int \int \left[\int_{\Omega(\mathbf{P}_0, \mathbf{p}, \delta)} F_1(t, \mathbf{R}_0, \mathbf{r}, \mathbf{P}_0, \mathbf{p}|\mathbf{R}') d\mathbf{r} \right] d\mathbf{p} d\mathbf{P}_0$$

which is direct analogue of function W_2 from [16] and satisfies

$$\int W_1(t, \Delta \mathbf{R}) d\Delta \mathbf{R} = c_1 = \nu_0 \bar{\Omega}(\delta)$$

Evidently, $W_1(t, \Delta \mathbf{R})$ is probability density of finding BP at point $\Delta \mathbf{R}$ (after start from coordinate origin) and simultaneously some atom in its close vicinity in some *in*-state or *out*-state of their mutual collision. Consequently, ratio

$$W_1(t, \Delta \mathbf{R})/V_0(t, \Delta \mathbf{R}) = \mathcal{P}_{post}(t, \Delta \mathbf{R})$$

presents a measure of conditional probability of BP's collision under condition that path $\Delta \mathbf{R}$ is known. The subscript “*post*” underlines that in essence this is a *posteriori* probability. In absence of historical correlations between BP and atoms we would have $W_1(t, \Delta \mathbf{R}) = c_1 V_0(t, \Delta \mathbf{R})$ and above ratio would reduce to unconditional *a priori* probability measure: $\mathcal{P}_{prior} = \nu_0 \bar{\Omega}(\delta)$.

In conventional kinetics, based on concepts like “probability of collision”, any difference between \mathcal{P}_{post} and \mathcal{P}_{prior} is unthinkable since it means dependence of “probability of collision” on wherefrom BP had started in former times. Therefore factual difference of \mathcal{P}_{post} from \mathcal{P}_{prior} , indicated by the virial relations, says that a random point process formed by BP' collisions is not a usual Poisson process. Then, what is it? The answer is rather obvious: it is Poisson process but supplied with such (relatively slow) scaleless random variations of “probability of collision” which exclude possibility to get it by time averaging. Indeed, on second thought it is clear that Poissonian statistics introduces “too strict disorder” in collisions to be likely.

Such interpretation of inter-particle correlations which keep safe even under BGL was expounded in [10, 11] (besides, it was in part developed in [13, 14, 15, 16], and its most principal aspects were anticipated already in [20, 21, 22, 23]). It was demonstrated that fluctuations in “probability of collision” (or, more precisely, relative frequency of collisions) possess scaleless 1/f-type spectrum (i.e. represent “1/f-noise”) and may be described also as 1/f fluctuations of BP's diffusivity (and mobility). Now we arrived at principally same results after start from virial relations.

Scaleless character of the fluctuations is due to fact that the system under consideration constantly forgets history of BP's collisions and therefore has neither stimulus nor means to force relative frequency of collisions to be certain. To keep it certain at arbitrary large time scales, the system, in opposite, should keep in mind arbitrary old history. In this sense, *a priori* equalization of \mathcal{P}_{post} and \mathcal{P}_{prior} acts as infinitely long memory. Notice that in comparison with Poissonian statistics of collisions a real one to some extent resembles Bose statistics.

Now let us compare \mathcal{P}_{post} and \mathcal{P}_{prior} . From section 3.5 it follows that sign of $V_1(t, \mathbf{R}_0, \mathbf{r}, \mathbf{P}_0, \mathbf{p}|\mathbf{R}')$ is determined by t and $\Delta \mathbf{R}$ only. Taking this into account, in the spirit of section 3.2 we can derive one more inequality,

$$\left| W_1(t, \Delta \mathbf{R}) - c_1 V_0(t, \Delta \mathbf{R}) - \frac{V_1(t, \Delta \mathbf{R})}{1 - \delta} \right| \leq \delta \left| \frac{V_1(t, \Delta \mathbf{R})}{1 - \delta} \right| \quad (52)$$

Being combined with (25) it implies that

$$\frac{\mathcal{P}_{post}(t, \Delta \mathbf{R})}{\mathcal{P}_{prior}} \leq 1 + \frac{1}{c_1} \frac{\partial \ln V_0(t, \Delta \mathbf{R})}{\partial \ln \nu_0} < 1 \quad (53)$$

when $\partial V_0(t, \Delta \mathbf{R})/\partial \nu_0 < 0$. When, in opposite, $\partial V_0(t, \Delta \mathbf{R})/\partial \nu_0 > 0$, then both inequality signs in (53) should be inverted.

Inequality (53) represents strengthened form of (25). At tails of $V_0(t, \Delta \mathbf{R})$ always $\partial V_0(t, \Delta \mathbf{R})/\partial \nu_0 < 0$, and it shows that, naturally, *a posteriori* probability of BP's collisions far enough at tails is smaller than *a priori* one.

Notice that if c_1 was an exact value, determined by minimum of all possible estimates of pair correlation volume (see section 3.6 and above), then middle expression in (53) would achieve its theoretical minimum too. Hence, in fact left inequality should be replaced by equality. Similar conclusion is valid also in respect to its alternative at $\partial V_0(t, \Delta \mathbf{R}) / \partial \nu_0 > 0$. Thus we can write

$$\frac{\mathcal{P}_{post}(t, \Delta \mathbf{R})}{\mathcal{P}_{prior}} = 1 + \frac{1}{c_1} \frac{\partial \ln V_0(t, \Delta \mathbf{R})}{\partial \ln \nu_0} = 1 - \frac{1}{c_1} \frac{\partial \ln V_0(t, \Delta \mathbf{R})}{\partial \ln D} \quad (54)$$

The last equality here relates to the Boltzmann-Grad gas. For distribution (2) or (48),

$$\frac{\mathcal{P}_{post}(t, \Delta \mathbf{R})}{\mathcal{P}_{prior}} \rightarrow \frac{7}{4} \left(1 + \frac{\Delta \mathbf{R}^2}{4Dt} \right)^{-1} \quad (55)$$

So substantial changeability of the *a posteriori* “probability of collision” shows that in fact this quantity has no certain value obtainable by time averaging.

4. Conclusion

Being guided by wrong idea of “statistical independency” of colliding particles (Boltzmann’s “molecular chaos”), classical gas kinetics neglected statistical inter-particle correlations which inevitably arise in spatially non-uniform Gibbsian statistical ensembles. Thus the concept of *a priori* definable “probability of collision” was unknowingly imposed on the theory as characteristics of a concrete particle trajectory. As for Brownian motion (self-diffusion) of gas particles, the result was “the law of large numbers” stating that probability distribution $V_0(t, \Delta \mathbf{R})$ of path of molecular Brownian particle (BP) is drawn towards the Gaussian distribution.

We derived exact virial expansion connecting response of $V_0(t, \Delta \mathbf{R})$ to gas perturbations, from one hand, and pair and many-particle “historical” statistical correlations between the BP’s path and gas, from the other hand. Specificity of “historical” correlations is that they are just products of initial spatial non-uniformity of an ensemble. Thus existence of such correlations is proved. At the same time, we showed that finiteness of spatial spread of these correlations is incompatible with Gaussian asymptotic of $V_0(t, \Delta \mathbf{R})$ even in dilute gas (under the Boltzmann-Grad limit). Then we demonstrated that the spread is really finite and, consequently, $V_0(t, \Delta \mathbf{R})$ has essentially non-Gaussian form, with power-law long tails (lasting up $|\Delta \mathbf{R}| \sim v_T t$). These results mean (i) that BP’s path can not be divided into “statistically independent” events or pieces, and, as combined with our previously published [10, 20, 21, 22] and unpublished [11, 13, 14, 15, 16] results, (ii) that “probability of collision” or, equivalently, diffusivity (and mobility) of BP in fact undergo scaleless fluctuations like the so-called 1/f-noise.

In principle, these conclusions extend to the kinetics as the whole. If applied to charge carriers in semiconductors, they naturally explain the “inherent 1/f-noise” under experimental investigation during many years [25, 26]. However, one has to revise kinetics of electron-phonon systems (as well as phonon systems themselves [27]), again removing from it *a priori* “probability of collision” and “statistical independencies”, and returning to honest analysis of infinite chains of many-particle statistical correlations. Perhaps, a time of such revision is not far off.

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References

- [1] Einstein A 1905 *Ann.Phys.* **17** 549
- [2] Einstein A 1906 Zur Theorie der Brownschen Bewegung *Ann.Phys.* **19** 371
- [3] Bernoulli Jacob and Sylla E D (translator) 2005 *Art of conjecturing* (John Hopkins University)
- [4] Boltzmann L 1896-1898 *Vorlesungen uber Gastheorie, Bd. 1 und 2* (Leipzig)
- [5] Bogolyubov N N 1962 *Problems of dynamical theory in statistical physics* (North-Holland)
- [6] Uhlenbeck O E and Ford G W 1963 *Lectures in statistical mechanics* (Providence: AMS)
- [7] Resibois P and de Leener M 1977 *Classical kinetic theory of fluids* (New-York: Wiley)
- [8] Balesku R 1997 *Statistical dynamics* (London: ICP)
- [9] Lifshitz E M and Pitaevski L P 1979 *Statistical Physics. Part II* (Moscow: Nauka)
- [10] Kuzovlev Yu E 1988 BBGKY equations, self-diffusion and 1/f-noise in slightly nonideal gas
Sov.Phys. - JETP **67** (12) 2469
- [11] Kuzovlev Yu E 1999 arXiv preprint cond-mat/9903350
- [12] Krylov N S 1979 *Works on the foundations of statistical physics* (Princeton)
- [13] Kuzovlev Yu E 2007 arXiv preprint 0710.3831
- [14] Kuzovlev Yu E 2007 Math. Physics Archive (University of Texas) preprint 07-309
- [15] Kuzovlev Yu E 2007 arXiv preprint 0705.4580
- [16] Kuzovlev Yu E 2006 arXiv preprint cond-mat/0609515
- [17] Bochkov G N and Kuzovlev Yu E 1977 *Sov.Phys.-JETP* **45** 125
- [18] Bochkov G N and Kuzovlev Yu E 1979 *Sov.Phys.-JETP* **49** 543
- [19] Bochkov G N and Kuzovlev Yu E 1981 *Physica A* **106** 443
- [20] Bochkov G N and Kuzovlev Yu E 1983 *Radiophysics and Quantum Electronics* No.3 [in Russian: *Izv. VUZov.-Radiofizika* **26** 310]
- [21] Bochkov G N and Kuzovlev Yu E 1984 *Radiophysics and Quantum Electronics* No.9 [in Russian: *Izv. VUZov.-Radiofizika* **27** 1151]
- [22] Bochkov G N and Kuzovlev Yu E 1983 *Physics-Uspekhi (Sov.Phys.-Usp.)* **26** 829
- [23] Bochkov G N and Kuzovlev Yu E 1985 On the theory of 1/f-noise *Preprint NIRFI No. 195* (USSR, Gorkii: NIRFI, in Russian)
- [24] Landau L L and Lifshitz E M 1976 *Statistical Physics. Part I* (Moscow: Nauka)
- [25] Hooge F N, Kleinpenning T G M and L.K.J. Vandamme L K J 1981 *Rep. Progr. Phys.* **44** 479
- [26] Toita M, Vandamme L K J et al. 2005 *Fluctuation and Noise Letters* **5** L539
- [27] Kuzovlev Yu E 1997 *JETP* 84(6) 1138